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# Pressure-stabilized hafnium nitrides and their properties

Jin Zhang,<sup>1,\*</sup> Artem R. Oganov,<sup>2,1,3,4,†</sup> Xinfeng Li,<sup>5</sup> and Haiyang Niu<sup>1</sup>

<sup>1</sup>*Department of Geosciences, Center for Materials by Design,  
and Institute for Advanced Computational Science,*

*State University of New York, Stony Brook, NY 11794-2100, USA*

<sup>2</sup>*Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 5 Nobel St., Moscow, 143026, Russia.*

<sup>3</sup>*International Center for Materials Discovery, School of Materials Science and Engineering,  
Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China*

<sup>4</sup>*Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region 141700, Russia*

<sup>5</sup>*State Key Laboratory for Mechanical Behavior of Materials,*

*School of Materials Science and Engineering, Xi'an Jiaotong University, Xian, 710049, PR China*

We report hafnium nitrides under pressure using first-principles evolutionary calculations. Metallic  $P6_3/mmc$ -HfN (calculated Vickers hardness 23.8 GPa) is found to be more energetically favorable than NaCl-type HfN at zero and high pressure. Moreover, NaCl-type HfN actually undergoes a phase transition to  $P6_3/mmc$ -HfN below 670 K at ambient pressure. Novel HfN<sub>10</sub>, which simultaneously has infinite armchair-like polymeric N-chains and N<sub>2</sub> molecules in its crystal structure, is discovered to be stable at moderate pressure above 23 GPa and can be preserved as a metastable phase at ambient pressure. At ambient conditions (298 K, 0 GPa), the gravimetric energy densities and the volumetric energy densities of HfN<sub>10</sub> are 2.8 kJ/g and 14.1 kJ/cm<sup>3</sup>, respectively.

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Nitrides of group IVB elements (Ti, Zr, Hf), which are widely used in industry, exhibit the attractive combination of various physical and chemical features. Among them, hafnium nitrides (HfN<sub>x</sub>), display high melting points (HfN: 3330 °C[1]), high incompressibility (HfN:  $B_0 = 260$ -306 GPa[2]; Hf<sub>3</sub>N<sub>4</sub>:  $B_0 = 227$ -260 GPa[3, 4]), oxidation resistance at high temperature[5] and superconductivity (HfN:  $T_c = 8.8$  K)[6], and have been widely exploited by experiments [7–10] and calculations[8–11] in recent years.

Three decades ago, Rudy[12] and Lengauer[13] observed and studied  $\epsilon$ -Hf<sub>3</sub>N<sub>2</sub> ( $R\bar{3}m$ ) and  $\zeta$ -Hf<sub>4</sub>N<sub>3</sub> ( $R\bar{3}m$ ) which were unstable above  $\sim 2000$  and  $\sim 2300$  °C, respectively. Compared with hafnium subnitrides, researchers put more efforts into studying the structures and properties of HfN and Hf<sub>3</sub>N<sub>4</sub>. Experimental effort[14] succeeded in growing single crystals of HfN by the zone-annealing technique and confirmed that metallic HfN crystallized in the rock-salt structure (B1) with a golden color. Theoretical investigations further indicated that NaCl (B1) type HfN will transform into CsCl (B2) type at a very high pressure (304 GPa[15] 246 GPa[8]).

In 1991, a transparent Hf<sub>3</sub>N<sub>4</sub> thin film had been prepared by chemical vapor deposition (CVD)[16] though at that time researchers were not certain about its exact crystal structure. Now, thin films of Hf<sub>3</sub>N<sub>4</sub> can also be deposited by atomic layer deposition (ALD)[17, 18]. Compared with the Hf<sub>3</sub>N<sub>4</sub> thin film, bulk Hf<sub>3</sub>N<sub>4</sub> is more difficult to prepare because of its high melting point. The transparent semiconducting or insulating bulk Th<sub>3</sub>P<sub>4</sub>-type Hf<sub>3</sub>N<sub>4</sub>( $I\bar{4}3d$ ), recoverable to ambient pressure, was synthesized by Zerr et al.[4] in laser-heated diamond anvil cells (LH-DACs) at pressures up to 18 GPa and temperatures up to 3,000 K. Subsequently, Salamat[7] crys-

tallized a tetragonal  $I4/m$ -Hf<sub>3</sub>N<sub>4</sub> polymorph at 12 GPa and 1500K and a high-pressure orthorhombic  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub> polymorph at 19 GPa and 2000 K using LH-DACs. Meanwhile, first-principles calculations[11, 15, 19] showed that orthorhombic  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub> was the most stable structure at ambient pressure and Th<sub>3</sub>P<sub>4</sub>-type Hf<sub>3</sub>N<sub>4</sub> was predicted to be stable above 9 GPa at 0 K[19].

Another motivation to study nitrogen compounds under pressure is that at impractically high pressures ( $>110$  GPa[20]) polymeric nitrogen is formed - the archetypal high-energy-density material (HEDM). Numerous theoretical[21–25] and experimental[26–28] studies tried to predict and synthesize polymeric forms of nitrogen or nitrogen-bearing compounds that can exist at ambient conditions. Virtually no works explored transition metal nitrides as a possibility to achieve polymerization of nitrogen at milder pressures.

Here, we not only report a theoretical pressure-composition phase diagram for Hf-N system, but also prove the existences of  $P6_3/mmc$ -HfN and found novel HfN<sub>10</sub> with polymeric nitrogen chains, as will be discussed below. The stable phases in the Hf-N system at pressure up to 60 GPa are searched by using first-principles evolutionary algorithm (EA) as implemented in the USPEX code[29–31] combined with *ab initio* structure relaxations using density functional theory (DFT) with the PBE-GGA functional[32], as implemented in the VASP package[33]. The electron-ion interaction was described by projector-augmented wave (PAW) potentials[34], with  $5p^66s^25d^2$  and  $2s^22p^3$  shells treated as valence for Hf and N, respectively. Subsequent calculation of phase transition and properties rely on well-converged structures (total energy convergence less than 1 meV/atom) with respect to the plane-wave

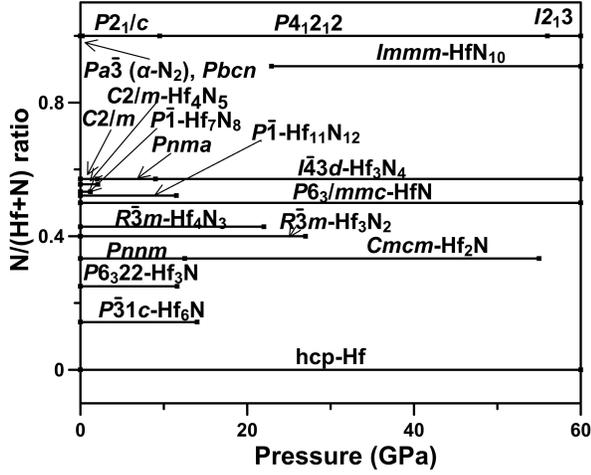


FIG. 1: Pressure-composition phase diagram of the Hf-N system.

energy cutoff (600 eV) and  $\Gamma$ -centered uniform  $k$ -meshes ( $2\pi \times 0.06 \text{ \AA}^{-1}$ ). For comparison and verification, local density approximation (LDA) is also used in calculating the free energy of some structures. Unless indicated otherwise calculations were done using the GGA. Phonon dispersions were calculated using the finite-displacement method in Phonopy code[35]. Voight-Reuss-Hill (VRH) approximation is adopted for estimating polycrystalline bulk modulus ( $B$ ) and shear modulus ( $G$ ).

Based on the global minimum of the free energy, we derived the pressure-composition phase diagram of the Hf-N system, as depicted in Fig. 1. Ten structures, including  $P\bar{3}1c$ -Hf<sub>6</sub>N,  $P6_322$ -Hf<sub>3</sub>N,  $Pnnm$ -Hf<sub>2</sub>N,  $R\bar{3}m$ -Hf<sub>3</sub>N<sub>2</sub>,  $R\bar{3}m$ -Hf<sub>4</sub>N<sub>3</sub>,  $P6_3/mmc$ -HfN,  $P\bar{1}$ -Hf<sub>11</sub>N<sub>12</sub>,  $P\bar{1}$ -Hf<sub>7</sub>N<sub>8</sub>,  $C2/m$ -Hf<sub>4</sub>N<sub>5</sub>,  $C2/m$ -Hf<sub>3</sub>N<sub>4</sub>, are stable at zero pressure (see Supplemental Material Table S1 for calculated structural parameters). All the other high-pressure Hf-N compounds can be decompressed to ambient conditions as metastable phases since they are mechanically and dynamically stable at 0 GPa (see Supplemental Material Fig. S2). The stoichiometries Hf<sub>6</sub>N and Hf<sub>3</sub>N were never reported by experiments, while previous MonteCarlo simulations[36] predicted the existence of Hf<sub>6</sub>N and Hf<sub>3</sub>N, and also indicated that the ground-state of Hf<sub>6</sub>N was  $P\bar{3}1c$ -Hf<sub>6</sub>N while the Hf<sub>3</sub>N belonged to  $R\bar{3}c$  or  $P6_322$ -Hf<sub>3</sub>N. Our calculations, with or without considering the zero point energy (ZPE), both not only showed that  $P\bar{3}1c$ -Hf<sub>6</sub>N is the most stable (note the free energy  $P\bar{3}1c$ -Hf<sub>6</sub>N is slightly lower than that of  $R\bar{3}c$ -Hf<sub>6</sub>N), but also indicated  $P6_322$ -Hf<sub>3</sub>N is more stable than  $R\bar{3}c$ -Hf<sub>3</sub>N at low pressures. Unlike  $P4_2/mnm$ -Ti<sub>2</sub>N (the stable phase for Ti<sub>2</sub>N at 0 GPa), Hf<sub>2</sub>N is more energetically favorable in an orthorhombic phase (space group:  $Pnnm$ ); this  $Pnnm$ -Hf<sub>2</sub>N transforms to  $Cmcm$ -Hf<sub>2</sub>N at

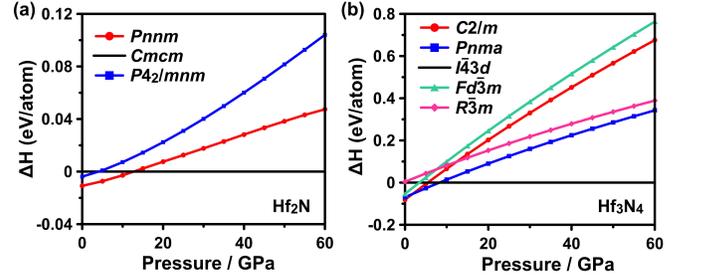


FIG. 2: (Color online) Enthalpy-pressure diagrams of Hf<sub>2</sub>N and Hf<sub>3</sub>N<sub>4</sub>.  $Cmcm$ -Hf<sub>2</sub>N and  $I\bar{4}3d$ -Hf<sub>3</sub>N<sub>4</sub> are taken as reference for Hf<sub>2</sub>N and Hf<sub>3</sub>N<sub>4</sub>, respectively.  $Fd\bar{3}m$ -Hf<sub>3</sub>N<sub>4</sub> belongs to spinel-type.

12.5 GPa and  $Cmcm$ -Hf<sub>2</sub>N continues to be stable up to 55 GPa (Fig. 2(a)). Experimental high-temperature structures  $R\bar{3}m$ -Hf<sub>3</sub>N<sub>2</sub> and  $R\bar{3}m$ -Hf<sub>4</sub>N<sub>3</sub> [12, 13] (experimental composition: Hf<sub>3</sub>N<sub>1.69</sub> and Hf<sub>4</sub>N<sub>2.56</sub>) are also found to be stable at lower pressures and will decompose at 27 GPa and 22 GPa, respectively.

Interesting and beyond the expectation, it turns out the ground state of HfN should be metallic  $P6_3/mmc$ -HfN instead of NaCl-type (B1) HfN which has been numerously reported in literature[8, 11, 19]. Note that the structure of our  $P6_3/mmc$ -HfN with 8 atoms in its unit cell is different from the NiAs-type HfN, which also has space group  $P6_3/mmc$ , with 4 atoms in its unit cell. The ground state B1 is 0.0187 eV/atom (without ZPE) or 0.0138 eV/atom (with ZPE) higher in energy than  $P6_3/mmc$ -HfN. In order to verify our calculations, as well as to compare with previous studies, relative enthalpies of  $P6_3/mmc$ -HfN and B1-HfN (without ZPE) are plotted up to 300 GPa in Fig. 3(a,c).  $P6_3/mmc$ -HfN is more stable than B1-HfN at all pressures up to 300 GPa and the transition between  $P6_3/mmc$ -HfN and CsCl-type (B2) HfN appears at 287 GPa (270 GPa in LDA). The transformation pressure from B1 to B2 is 275 GPa (258 GPa in LDA), which is comparable with previous GGA result of 301 GPa[15].

$P6_3/mmc$ -HfN actually consists of a double close packed hexagonal (dhcp) lattice of Hf atoms, with nitrogen atoms filling all octahedral voids, as seen in Fig. 4(a). Hf-N covalent bond can be revealed by the hybridization between the Hf-d and N-p orbitals in Fig. 4(b); Hf-Hf and Hf-N bonding characters can be reflected by calculating crystal orbit Hamilton population (COHP)[37] using the TB-LMTO-ASA program[38]. Based on the quasi-harmonic approximation (QHA),  $P6_3/mmc$ -HfN will transform into B1-HfN at 670 K (397 °C) as shown in Fig. 3(e).

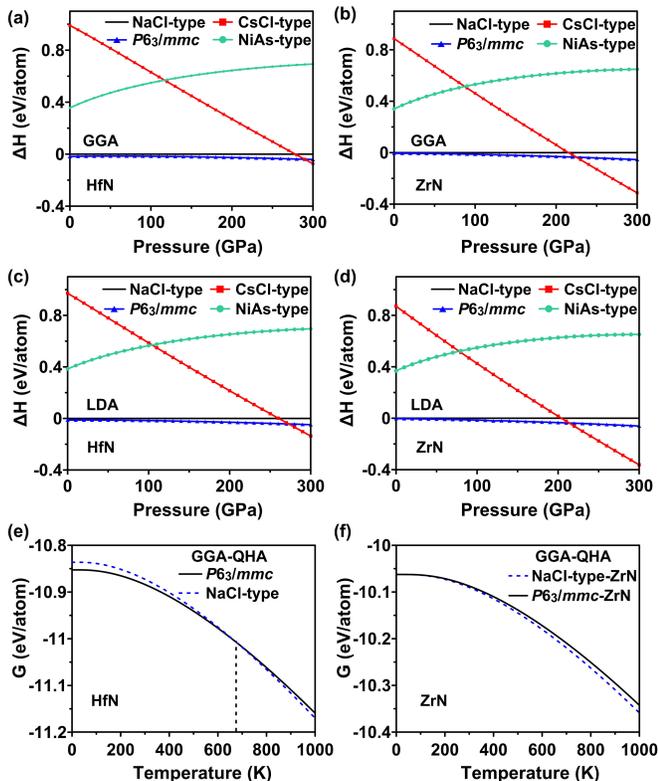


FIG. 3: (Color online) Enthalpy-pressure diagrams of HfN and ZrN in (a,b) GGA and (c,d) LDA, respectively (relative to the NaCl-type HfN and NaCl-type ZrN), (e,f) free enthalpy as a function of temperature of  $P6_3/mmc$  and NaCl-type structures for HfN and ZrN obtained by the quasi-harmonic approximation (QHA) method and the GGA.

Ti and Zr are in the same group with Hf, and especially Zr has strong chemical similarity with Hf. The existence of the new hexagonal HfN naturally leads to the question as to whether similar structures can exist for TiN and ZrN. Thus we computed the enthalpy-pressure diagrams of ZrN and TiN in the GGA and LDA. For the enthalpy-pressure diagram of TiN (without ZPE, see Supplemental Material Fig. S3), the ground state energy of  $P6_3/mmc$ -TiN is 0.0344 eV/atom higher than that of B1-TiN, thus B1-TiN is still the most stable structure at 0 GPa. The case of ZrN is tricky. As shown in Table I,  $P6_3/mmc$ -ZrN is 0.0052 eV/atom (without ZPE) higher than B1-ZrN in free energy while B1-ZrN is 0.0006 eV/atom energetically higher than  $P6_3/mmc$ -ZrN with ZPE. This is not surprising, because the ZPE for  $P6_3/mmc$ -HfN and B1-HfN are 0.0625 and 0.0572 eV/atom respectively, for  $P6_3/mmc$ -ZrN and B1-ZrN is 0.0642 eV/atom and 0.0584 eV/atom respectively; along with the energy difference (0.0052 eV/atom, without ZPE) between  $P6_3/mmc$ -ZrN and B1-ZrN is too small compared with the energy difference (0.0186 eV/atom, without ZPE) between  $P6_3/mmc$ -HfN

TABLE I: Calculated lattice parameters  $a$  and  $c$ , bulk modulus  $B_0$ , its pressure derivation  $B'_0$  (calculated parameters were fit to a third-order Birch-Murnaghan equation of state), equilibrium volume  $V_0$ , free energy without ZPE  $E$  and free energy with ZPE  $E_0$ .

Parameter	HfN		ZrN	
	$P6_3/mmc$	B1	$P6_3/mmc$	B1
$a$ (Å)	3.1791	4.5373	3.2349	4.6169
$c$ (Å)	10.6976		10.8626	
$B_0$ (GPa)	265.37	270.16	245.04	247.91
$B'_0$	4.255	4.289	4.239	4.282
$V_0$ (Å <sup>3</sup> )	93.63	93.41	98.45	98.41
$E$ (eV/atom)	-10.9126	-10.8940	-10.1259	-10.1207
$E_0$ (eV/atom)	-10.8501	-10.8368	-10.0617	-10.0623

and B1-HfN; so when the ZPE is considered, B1-ZrN becomes more stable than  $P6_3/mmc$ -ZrN. The computed Gibbs free energies (Fig. 3(f)) show that we can not expect  $P6_3/mmc$ -ZrN will like  $P6_3/mmc$ -HfN become stable at ambient conditions. However, with increasing pressure,  $P6_3/mmc$ -ZrN becomes more stable than B1-ZrN, see Fig. 3(b,d). The transition pressure from  $P6_3/mmc$ -ZrN to B2-ZrN is 221 GPa (212 in LDA), and the value of the metastable transition pressure from B1-ZrN to B2-ZrN is 211 GPa (201 in LDA), which is in accordance with previous GGA calculations: 205 GPa from Hao's work[39] and 208 GPa from Kroll's work[15].

Based on our calculations, we can theoretically conclude that for  $P6_3/mmc$ -TiN,  $P6_3/mmc$ -ZrN and  $P6_3/mmc$ -HfN, only  $P6_3/mmc$ -HfN is stable at the ambient conditions. However, why  $P6_3/mmc$ -HfN is never experimentally found? Seen from the Hf-N equilibrium diagram, NaCl-type HfN appears above 500 °C[40]. In fact, experiments which tried to synthesize HfN crystal, HfN films or HfN powder, always operated at temperatures above 400 °C. A single crystal of HfN was grown by zone annealing technique with a temperature approximately 2500 °C[14]. Fabricating HfN film by chemical vapor deposition (CVD) generally needs to take place at high temperatures above 1000 °C[16]; physical vapor deposition (PVD)-reactive sputtering is also used to synthesize HfN at 450 °C[41]. At room temperature, hafnium nitride films can be formed by ion beam synthesis[42], but these hafnium nitride films are a mixture  $Hf_3N_2$ ,  $Hf_4N_3$  and HfN.

Three metallic Hf-vacancy nitrides, including  $P\bar{1}$ - $Hf_{11}N_{12}$ ,  $P\bar{1}$ - $Hf_7N_8$  and  $C2/m$ - $Hf_4N_5$  are stable at 0 GPa, consistent with the stoichiometries proposed by experiments of Hf-vacancies containing in  $HfN_x$  film ( $x > 1$ )[9, 10]. The ground-state phase we find for  $Hf_3N_4$  is not the orthorhombic  $Zr_3N_4$ -type ( $Pnma$ ) which was proposed[15, 19] earlier. Instead, a monoclinic  $C2/m$ -

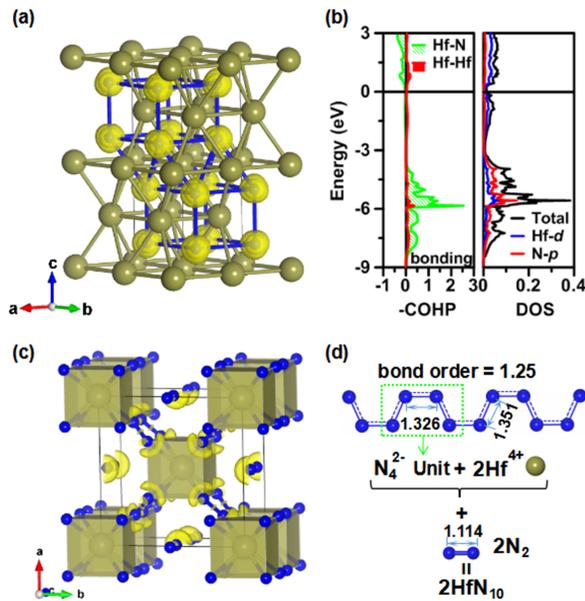


FIG. 4: (Color online) ELF isosurface (ELF = 0.85) of (a)  $P6_3/mmc$ -HfN and (c)  $Immm$ -HfN<sub>10</sub> at 0 GPa, (b) density of states and -COHP for  $P6_3/mmc$ -HfN, (d) the composition illustration of  $Immm$ -HfN<sub>10</sub> (the bond length is in Å). Hf-centered polyhedra are dark yellow; part of the infinite N chain and N≡N bonds are also displayed in (d). Large grey spheres-Hf atoms; small blue spheres-N atoms.

Hf<sub>3</sub>N<sub>4</sub> is more energetically favorable than  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub>. With increasing pressure, two transitions occur in Hf<sub>3</sub>N<sub>4</sub>:  $C2/m$ -Hf<sub>3</sub>N<sub>4</sub> →  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub> at 2 GPa and  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub> → Th<sub>3</sub>P<sub>4</sub>-type Hf<sub>3</sub>N<sub>4</sub> at 9 GPa (Fig. 2(b)).

Another interesting metallic structure  $Immm$ -HfN<sub>10</sub> with every Hf atom coordinated by 8 N atoms, is stable at pressures above 23 GPa. This structure simultaneously contains encapsulated N<sub>2</sub> molecules with the triple N≡N bonds (bond length is 1.114 Å) and infinite polymeric N chain. Electrons are delocalized over the whole infinite polymeric N chains. Each N-N bond in the infinite polymeric N chain is an intermediate bond between single and double bonds, as shown in Fig. 4(d). In addition, we find that  $Immm$ -ZrN<sub>10</sub> and  $Immm$ -TiN<sub>10</sub> can also be metastable structures (dynamically and mechanically stable) at ambient pressure. The gravimetric energy density for  $Immm$ -TiN<sub>10</sub> is 5.2 kJ/g at ambient conditions (298 K, 0GPa), higher than that for the well-known explosive material TNT (4.3 kJ/g) and mildly lower than another powerful explosive HMX (5.7 kJ/g)[43]. Gravimetric energy densities for  $Immm$ -HfN<sub>10</sub> and  $Immm$ -ZrN<sub>10</sub> are 2.8 kJ/g and 3.6 kJ/g at ambient conditions, respectively. And the volumetric energy densities of HfN<sub>10</sub>, ZrN<sub>10</sub> and TiN<sub>10</sub> are correspondingly 14.1 kJ/cm<sup>3</sup>, 12.9 kJ/cm<sup>3</sup> and 16.4 kJ/cm<sup>3</sup> (see Supplemental Material for detailed energy density calculations),

TABLE II: Pressure range (PR) of stability of Hf-N compounds and their calculated zero-pressure elastic properties (polycrystalline bulk modulus  $B$ , shear modulus  $G$ , Young's modulus  $E$ , Poisson's ratio  $\nu$  and Vickers hardness).  $G/B$  and  $\nu$  are dimensionless; PR,  $B$ ,  $G$ ,  $E$  and  $H_v$  are in GPa.

Compound	PR	$B_H$	$G_H$	$E$	$G/B$	$\nu$	$H_v$
$P31c$ -Hf <sub>6</sub> N	0-14	128.4	68.8	175.1	0.54	0.273	8.4
$P6_322$ -Hf <sub>3</sub> N	0-11.6	154.8	79.6	204.0	0.51	0.281	8.9
$Pnmm$ -Hf <sub>2</sub> N	0-12.5	189.4	113.3	283.4	0.60	0.251	14.4
$Cmcm$ -Hf <sub>2</sub> N	12.5-55	170.1	106.0	263.2	0.62	0.242	14.6
$R\bar{3}m$ -Hf <sub>3</sub> N <sub>2</sub>	0-27	212.5	134.5	333.2	0.63	0.238	17.6
$R\bar{3}m$ -Hf <sub>4</sub> N <sub>3</sub>	0-22	223.0	131.1	328.8	0.59	0.254	15.6
$P6_3/mmc$ -HfN	0-60	264.1	180.6	441.3	0.68	0.221	23.8
NiAs type-HfN		242.5	128.8	328.3	0.53	0.274	13.4
NaCl-type-HfN		267.9	163.0	406.5	0.61	0.247	19.0
$P\bar{1}$ -Hf <sub>11</sub> N <sub>12</sub>	0-11.5	259.4	176.2	431.0	0.68	0.223	23.2
$P\bar{1}$ -Hf <sub>7</sub> N <sub>8</sub>	0-1.2	253.0	173.4	423.5	0.69	0.221	23.2
$C2/m$ -Hf <sub>4</sub> N <sub>5</sub>	0-2.1	235.5	162.2	395.7	0.69	0.226	22.4
$C2/m$ -Hf <sub>3</sub> N <sub>4</sub>	0-2	225.5	159.0	386.1	0.71	0.214	22.8
$Pnma$ -Hf <sub>3</sub> N <sub>4</sub>	2-9	208.4	100.5	259.8	0.48	0.292	9.6
$I\bar{4}3d$ -Hf <sub>3</sub> N <sub>4</sub>	9-60	216.0	124.5	313.4	0.58	0.258	14.7
$Immm$ -HfN <sub>10</sub>	23-60	150.4	94.8	235.0	0.63	0.240	13.7

which are higher than TNT (7.2-8.0 kJ/cm<sup>3</sup>), RDX (10.1 kJ/cm<sup>3</sup>) and PETN (10.6 kJ/cm<sup>3</sup>)[44, 45].

The elastic moduli of all the Hf-N compounds are calculated according to the elastic constants tensors and theoretical hardnesses can be further predicted based on the Chen-Niu's empirical correlation [46] as listed in Table II.  $P6_3/mmc$ -HfN exhibits the highest shear modulus (180.6 GPa) and its calculated hardness is 23.8 GPa. It is worthwhile to note that Hf-vacancy containing structures, including  $P\bar{1}$ -Hf<sub>11</sub>N<sub>12</sub>,  $P\bar{1}$ -Hf<sub>7</sub>N<sub>8</sub>,  $C2/m$ -Hf<sub>4</sub>N<sub>5</sub> and  $C2/m$ -Hf<sub>3</sub>N<sub>4</sub>, also show high hardnesses. The  $G/B$  ratio, proposed by Pugh[47], can be used to judge the brittleness and ductility of materials:  $G/B > 0.57$  corresponds to brittle and  $G/B < 0.57$  to ductile behavior.  $C2/m$ -Hf<sub>3</sub>N<sub>4</sub> is the most brittle, while  $Pnma$ -Hf<sub>3</sub>N<sub>4</sub> is the most ductile among the Hf-N compounds. Moreover,  $G/B$  can also represent the directionality of bonding in the material[48].  $P6_3/mmc$ -HfN and  $C2/m$ -Hf<sub>3</sub>N<sub>4</sub> have a strong covalent (directional) component of bonding which has a positive effect on their hardnesses. Increasing the nitrogen content in subnitrides can improve their mechanical properties due to the formation of additional Hf-N bonds. For nitrogen-rich compounds, the effect of nitrogen content to mechanical properties is minor and atomic configuration becomes the main factor determining the mechanical properties.

In summary, we predicted the pressure-composition phase diagram of the Hf-N system. Several novel phases and new stoichiometries are found. Metallic  $P6_3/mmc$ -HfN with the highest hardness (23.8 GPa) among Hf-N compounds should be the ground state for HfN and will transform into NaCl-HfN at 670 K at ambient pressure.

Semiconducting  $C2/m\text{-Hf}_3\text{N}_4$  has lower energy than previously proposed  $Pnma\text{-Hf}_3\text{N}_4$  at 0 GPa. The calculated hardnesses of all the predicted high-pressure Hf-N phases range from 8.4 to 23.8 GPa at 0 GPa. It is noteworthy that Hf-vacancies do not degrade the mechanical properties of nitrides, e.g. both  $\text{Hf}_7\text{N}_8$  and  $\text{Hf}_{11}\text{N}_{12}$  exhibit good hardness.  $\text{HfN}_{10}$ , containing polymeric nitrogen chains, is predicted to become stable at the pressure above 23 GPa. Meanwhile it is a potential high-energy-density material because of its good gravimetric (2.8 kJ/g) and volumetric energy densities (14.1 kJ/cm<sup>3</sup>). This work provides an important guide for the experiment to synthesize  $\text{HfN}_{10}$ , an analog of polymeric nitrogen, at a moderate pressure and  $\text{HfN}_{10}$  also has a possibility to be kept as metastable phase at ambient pressure based on our analysis.

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\* Electronic address: Jin.Zhang.1@stonybrook.edu

† Electronic address: artem.oganov@stonybrook.edu

- [1] M. Wittmer, *J. Vac. Sci. Technol., A* **3**, 1797 (1985).
- [2] X.-J. Chen, V. V. Struzhkin, Z. Wu, M. Somayazulu, J. Qian, S. Kung, A. N. Christensen, Y. Zhao, R. E. Cohen, H.-k. Mao, *et al.*, *Proc. Natl. Acad. Sci. USA* **102**, 3198 (2005).
- [3] D. A. Dzivenko, A. Zerr, R. Boehler, and R. Riedel, *Solid State Commun.* **139**, 255 (2006).
- [4] A. Zerr, G. Miehe, and R. Riedel, *Nat. Mater.* **2**, 185 (2003).
- [5] M. M. Opeka, I. G. Talmy, E. J. Wuchina, J. A. Zaykoski, and S. J. Causey, *J. Eur. Ceram. Soc.* **19**, 2405 (1999).
- [6] H. O. Pierson, *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps.* (William Andrew, 1996).
- [7] A. Salamat, A. L. Hector, B. M. Gray, S. A. Kimber, P. Bouvier, and P. F. McMillan, *J. Am. Chem. Soc.* **135**, 9503 (2013).
- [8] M. Chauhan and D. C. Gupta, *Int. J. Refract. Met. Hard Mater.* **42**, 77 (2014).
- [9] C. Hu, Z. Gu, J. Wang, K. Zhang, X. Zhang, M. Li, S. Zhang, X. Fan, and W. Zheng, *J. Phys. Chem. C* **118**, 20511 (2014).
- [10] Z. Gu, C. Hu, H. Huang, S. Zhang, X. Fan, X. Wang, and W. Zheng, *Acta Mater.* **90**, 59 (2015).
- [11] H. Huang, X. Fan, C. Hu, D. J. Singh, Q. Jiang, and W. Zheng, *J. Phys.: Condens. Matter* **27**, 225501 (2015).
- [12] E. Rudy, *Metall. Mater. Trans.* **1**, 1249 (1970).
- [13] W. Lengauer, D. Rafaja, G. Zehetner, and P. Ettmayer, *Acta Mater.* **44**, 3331 (1996).
- [14] A. N. Christensen, W. Kress, M. Miura, and N. Lehner, *Phys. Rev. B* **28**, 977 (1983).
- [15] P. Kroll, *J. Phys.: Condens. Matter* **16**, S1235 (2004).
- [16] R. Fix, R. G. Gordon, and D. M. Hoffman, *Chem. Mater.* **3**, 1138 (1991).
- [17] K. Y. Ahn and L. Forbes, "Atomic layer deposition of  $\text{Hf}_3\text{N}_4/\text{HfO}_2$  films as gate dielectrics," (2009), US Patent 7,498,247.
- [18] J. S. Becker, E. Kim, and R. G. Gordon, *Chem. Mater.* **16**, 3497 (2004).
- [19] P. Kroll, *Phys. Rev. Lett.* **90**, 125501 (2003).
- [20] M. I. Eremets, R. J. Hemley, H.-k. Mao, and E. Gregoryanz, *Nature* **411**, 170 (2001).
- [21] W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, *Phys. Rev. Lett.* **93**, 125501 (2004).
- [22] F. Zahariev, A. Hu, J. Hooper, F. Zhang, and T. Woo, *Phys. Rev. B* **72**, 214108 (2005).
- [23] Y. Yao, J. S. Tse, and K. Tanaka, *Phys. Rev. B* **77**, 052103 (2008).
- [24] Y. Ma, A. R. Oganov, Z. Li, Y. Xie, and J. Kotakoski, *Phys. Rev. Lett.* **102**, 065501 (2009).
- [25] H. Yu, D. Duan, F. Tian, H. Liu, D. Li, X. Huang, Y. Liu, B. Liu, and T. Cui, *J. Phys. Chem. C* **119**, 25268 (2015).
- [26] M. I. Eremets, A. G. Gavriluk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, *Nat. Mater.* **3**, 558 (2004).
- [27] I. Trojan, M. Eremets, S. Medvedev, A. Gavriluk, and V. Prakapenka, *Appl. Phys. Lett.* **93**, 091907 (2008).
- [28] D. Tomasino, M. Kim, J. Smith, and C.-S. Yoo, *Phys. Rev. Lett.* **113**, 205502 (2014).
- [29] A. R. Oganov and C. W. Glass, *J. Chem. Phys.* **124**, 244704 (2006).
- [30] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, *Comput. Phys. Commun.* **184**, 1172 (2013).
- [31] A. R. Oganov, A. O. Lyakhov, and M. Valle, *Acc. Chem. Res.* **44**, 227 (2011).
- [32] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [33] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [34] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [35] A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).
- [36] A. V. Ruban, V. I. Baykov, B. Johansson, V. V. Dmitriev, and M. S. Blanter, *Phys. Rev. B* **82**, 134110 (2010).
- [37] R. Dronskowski and P. E. Bloechl, *J. Phys. Chem.* **97**, 8617 (1993).
- [38] G. Krier, O. Jepsen, A. Burkhardt, and O. Andersen, *Stuttgart* (1995).
- [39] A. Hao, T. Zhou, Y. Zhu, X. Zhang, and R. Liu, *Mater. Chem. Phys.* **129**, 99 (2011).
- [40] H. Okamoto, *J. Phase Equilib.* **11**, 146 (1990).
- [41] S. Shinkai and K. Sasaki, *Jpn. J. Appl. Phys.* **38**, 2097 (1999).
- [42] A. Arranz, *Surf. Sci.* **563**, 1 (2004).
- [43] B. Dobratz and P. Crawford, *LLNL Handbook of Explosives, UCRL-52997, Lawrence Livermore National Laboratory* (1985).
- [44] D. W. Smith, S. T. Iacono, and S. S. Iyer, *Handbook of fluoropolymer science and technology* (John Wiley & Sons, 2014).
- [45] K. S. Martirosyan, *J. Mater. Chem.* **21**, 9400 (2011).
- [46] X.-Q. Chen, H. Niu, D. Li, and Y. Li, *Intermetallics* **19**, 1275 (2011).
- [47] S. Pugh, *Philos. Mag.* **45**, 823 (1954).

- [48] K. Tanaka, K. Okamoto, H. Inui, Y. Minonishi, M. Yamaguchi, and M. Koiwa, *Philos. Mag. A* **73**, 1475 (1996).